

Synthesis, Characterization and Structural Transformation of A Condensed Rare Earth Metal Coordination Polymer

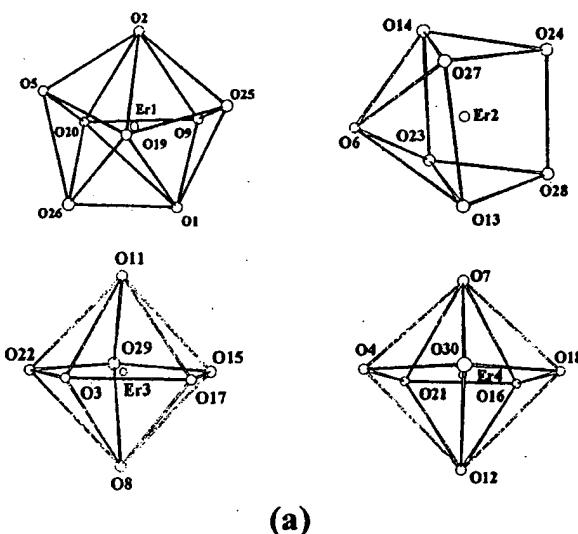
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There has been tremendous interest in the synthesis and crystal structure of open-framework materials due to their potential applications in catalysis, separations, and ion exchange processes.¹ A variety of organic molecules, including bi-, tri-, and tetradentate (diamondoid) ligands,² have been used in the construction of many fascinating structures. 1,4-Benzenedicarboxylic acid (H_2BDC), a rodlike bifunctional ligand, has afforded a number of extended structures by virtue of an exodentate coordination mode.³ An interesting lanthanide–BDC system has been reported recently that consists of a microporous structure generated upon removal of water from a condensed phase. This system is potentially important as a fluorescent probe.⁴

Our previous studies on dicarboxylic acids have shown that they are highly reactive toward metals under hydrothermal conditions.⁵ In this work, 1,4-benzenedicarboxylic acid has been selected as a ligand and a water/ethanol solution as a solvent. Hydrated $Er(NO_3)_3$ (0.075 g), H_2BDC (0.036 g), H_2O (10 mL), and EtOH (1 mL) in the mole ratio of 1:1.2645:83 were placed in a 23 mL acid digestion bomb and heated at 160 °C for 3 days. The pH of the final solution was 4.5. The pink crystals of $Er_4(BDC)_6 \cdot 6H_2O$ (1) (0.074 g, 74.2%) were collected after washing by water (3 × 10 mL) and by acetone (3 × 10 mL), respectively.^{6a} A microcrystalline sample of $Er_4(BDC)_6$ (2) resulted after 1 (23



(a)

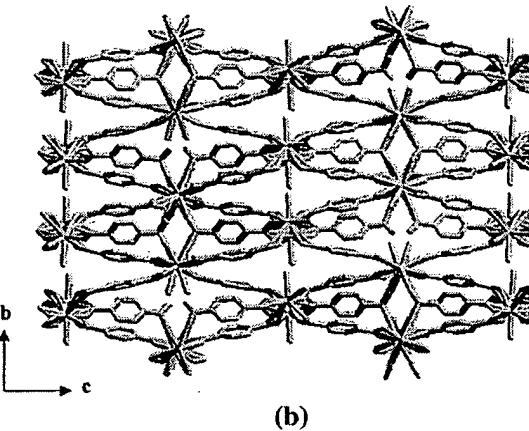


Figure 1. (a) Coordination polyhedra for the four crystallographically independent Er ions in 1. (b) A perspective view of the crystal structure of 1 along the a -axis. Er¹, Er², Er³, and Er⁴ are crystallographically equivalent to Er¹, Er², Er³, and Er⁴, respectively.

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- (6) (a) Found (calcd) for $Er_4O_{30}C_{48}H_{36}$ (1): C, 32.59 (32.72); H, 1.95 (2.06). The purity of the bulk sample was confirmed by comparison of the observed and calculated PXRD patterns. FT-IR (KBr): $\nu_{as}(COO^-) = 1554.6\text{ cm}^{-1}$, $\nu_s(COO^-) = 1418.6\text{ cm}^{-1}$. It does not dissolve in common organic solvents such as benzene, diethyl ether, acetonitrile, *N,N*-dimethylformamide, and dimethyl sulfoxide. (b) Found (calcd) for $Er_4O_{24}C_{48}H_{24}$ (2): C, 34.71 (34.86); H, 1.43 (1.47). (c) Found (calcd) for $Er_2O_{16}C_{24}H_{20}$ (3): C, 32.11 (32.06); H, 2.43 (2.25). (d) Found (calcd) for $Er_2O_{16}C_{24}H_{20}$ (3) following the preparation procedure described in ref 4: C, 32.09 (32.06); H, 2.30 (2.25).

mg) was heated to 300 °C under nitrogen gas.^{6b} A thermogravimetric (TG) curve indicated clearly the weight loss of six water molecules. $Er_2(BDC)_3 \cdot 4H_2O$ (3) was obtained by allowing 2 to be exposed to saturated water vapor for 2 h.^{6c} This structural transformation was confirmed by PXRD, IR, and elemental microanalysis. 3 is isostructural to $Tb_2(BDC)_3 \cdot 4H_2O$ ⁴ and can also be prepared using the same method described in ref 4.^{6d}

The crystal structure of 1 is a condensed three-dimensional network.⁷ There are four crystallographically independent erbium ions in this structure. The local coordination geometry around

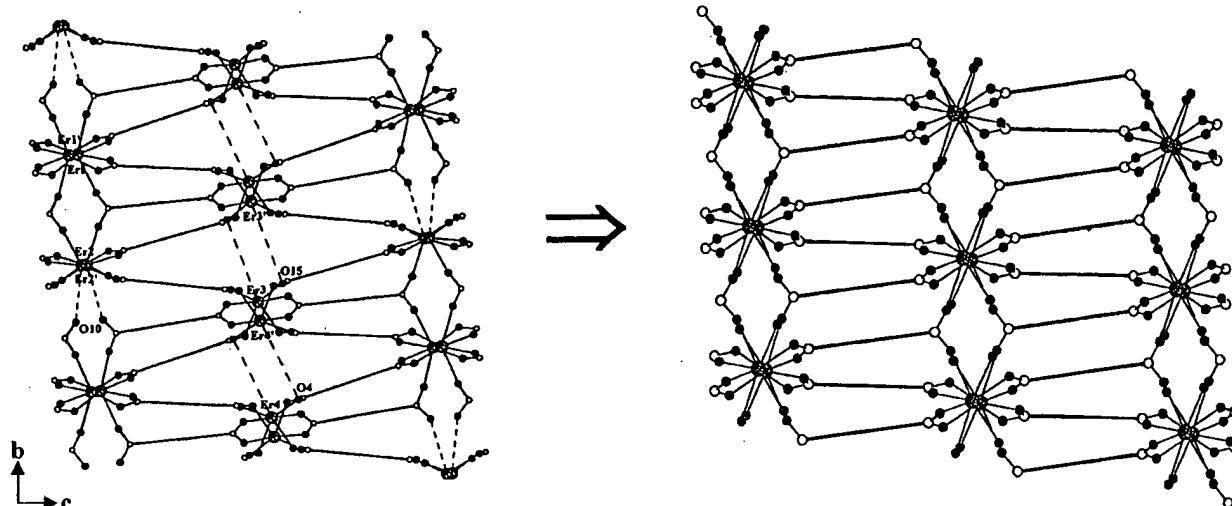


Figure 2. Structural transformation from $\text{Er}_4(\text{bdc})_6 \cdot 6\text{H}_2\text{O}$ (1, left) to $\text{Er}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$ (3, right). Water molecules are omitted in both structures for clarity.

Er1 is a dodecahedron which consists of six oxygen atoms from six bdc and two from water molecules. The coordination polyhedron around **Er2** is a capped trigonal prism which contains five carboxylate oxygen and two water oxygen atoms. The coordination environments of **Er3** and **Er4** are both pentagonal bipyramidal. The pentagonal planes are composed of four carboxylate oxygen atoms and a water oxygen atom, and the two apical sites are taken by another two carboxylate oxygen atoms (Figure 1a). A perspective view of the structure along the a -axis is illustrated in Figure 1b. All **Er1** and **Er2** are located in one plane whereas all **Er3** and **Er4** are located in the other plane (Figure 2, left side). The separation between the adjacent planes is 9.5 Å. The neighboring **Er1** and **Er1'** (or **Er2** and **Er2'**) atoms are approximately parallel to the c -axis and they are connected by two carboxylic groups from the two bridging bdc ligands,⁸ whereas **Er1** and **Er2** are approximately parallel to the b -axis and are connected by one carboxylic group through a bridging bdc. There are no direct connections between the **Er3** and **Er3'** (or **Er4** and **Er4'**) atoms. The neighboring **Er3** and **Er4** atoms are connected by three carboxylic groups of three different bridging bdc ligands. There are two μ_4 and one μ_3 coordination modes for bdc. Each of the two μ_4 -bdc bridges to four erbium ions through its four carboxylate oxygen atoms,⁹ and the μ_3 -bdc bonds only to three metals using three of its carboxylate oxygen atoms. A comparison of this structure with that of $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$ reveals the differences in the two: While metal ions form a single type of dodecahedron in $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$, there are three different coordination polyhedra for Er in **1**. Similarly, the bdc utilizes two bonding modes in the former structure while it utilizes three in the latter. Following the same procedure described in ref 4, we successfully isolated $\text{Er}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$ (**3**) by replacing Tb (or Eu) salt with erbium nitrate, which is isostructural to $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$. The formation of **3** was confirmed by PXRD. Attempts to synthesize **1** under hydrothermal conditions in water failed. This

suggests that the existence of ethanol was crucial for the formation of **1**. The strong adsorption peaks at $\nu_{as}(\text{COO}^-) = 1554.6 \text{ cm}^{-1}$ and $\nu_s(\text{COO}^-) = 1418.6 \text{ cm}^{-1}$ in the IR spectrum of **1** showed that carboxylate groups of bdc coordinate to erbium ions in a bridging fashion.⁹ This is in agreement with the result of the X-ray structure analysis. **1** is more condensed than $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$. The unoccupied volume was calculated to be 20.41% for **1**, based on the unit cell volume, and 21.17% for $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$.

Thermogravimetric analysis (TGA) study revealed that **1** underwent a two-step decomposition process, with its first weight loss occurring at 90–133 °C. The weight lost corresponded to six water molecules per formula unit (found 6.3%, calcd 6.1%). Increasing temperature led to the decomposition of the compound at 510 °C. The final pyrolysis was completed at 800 °C, giving a pink powder of Er_2O_3 . Having a flat plateau from 133 to 510 °C (a span of nearly 400 °C), **1** represents one of the most stable coordination polymers encountered so far.¹⁰ Reabsorption of water was probed after **1** lost six water molecules. The IR spectrum of **2**, the sample after the total removal of water at 300 °C, reveals that the broad peak around 3500–3450 cm^{-1} originally assigned to water molecules in **1** disappeared, and the strong peaks $\nu_{as}(\text{COO}^-)$ at 1539.2 cm^{-1} and $\nu_s(\text{COO}^-)$ at 1426.4 cm^{-1} confirmed the shift of Er–O (metal–carboxylate oxygen) stretches. A comparison on the PXRD patterns of **1** (Figure 3a) and **2** (Figure 3b) also shows significant shifting, broadening, and possibly splitting of some diffraction lines. To our surprise, the PXRD pattern (Figure 3c) of the sample after exposure of **2** to saturated water vapor for 2 h gave an almost perfect match to that of **3** prepared following the procedures described in ref 4 (Figure 3d). The IR spectra of these two samples were almost identical.

In structure **1**, the distances between **Er2** and **O10** are 4.838–4.854 Å. Upon heating and removal of water from the compound, the structure (**2**) will contract as indicated by the COO^- vibration shift in IR. Simultaneously, the uncoordinated **O10** atoms will be highly subject to bonding to the adjacent, unsaturated **Er2**, resulting in a similar coordination geometry for both **Er1** and **Er2** as in $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$. On the other hand, the holes in **2** between **Er3** and **Er4** will collapse due to the unstable pentagonal coordination of **Er3** and **Er4** after removal of the two coordinated

(7) Pink needle crystals of $\text{Er}_4(\text{bdc})_6 \cdot 6\text{H}_2\text{O}$ were analyzed at 298 K: orthorhombic, space group $Pbca$, $a = 9.661(2) \text{ \AA}$, $b = 26.224(3) \text{ \AA}$, $c = 37.863(3) \text{ \AA}$, $V = 9593(3) \text{ \AA}^3$, $Z = 8$, $D_c = 2.440 \text{ g/cm}^3$, and $\mu(\text{Mo K}\alpha) = 71.25 \text{ cm}^{-1}$. Data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo K α radiation. The unit cell parameters for data collection were measured by least-squares analysis of the setting angles of 25 well-centered reflections with $14.57^\circ \leq \theta \leq 18.66^\circ$. A total of 10379 reflections were measured, of which 6288 were observed with $I \geq 3.0a(I)$ and these were used in structure solution and refinement; $R = 0.045$, $R_w = 0.058$, GOF = 1.38. The structure was solved and refined using the TEXSAN package.

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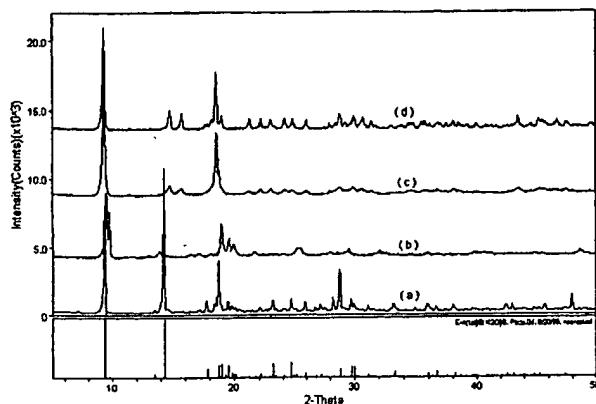


Figure 3. (a) Observed PXRD pattern for crystalline solid $\text{Er}_4(\text{bdc})_6 \cdot 6\text{H}_2\text{O}$ (**1**). (b) Observed PXRD pattern of $\text{Er}_4(\text{bdc})_6$ (**2**) after removal of six waters in **1**. (c) Observed PXRD pattern of the rehydrated sample after powders of **2** were placed in saturated water for 2 h. (d) PXRD pattern of $\text{Er}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$ (**3**) synthesized following the procedure described in ref 4. Bottom: calculated PXRD pattern for **1** from single-crystal data.

water molecules. A reasonable assumption is that such an instability may force the structure to reorganize by breaking the $\text{Er}^3-\text{O}15$ and $\text{Er}^4-\text{O}4$ bonds and forming new bonds between

$\text{Er}^3-\text{O}15$ and $\text{Er}^4-\text{O}4$, resulting in a $\text{Tb}_2(\text{bdc})_3 \cdot 4\text{H}_2\text{O}$ type structure (Figure 2, right). Structure rearrangement of this type has been observed only in a few coordination polymers.¹¹ A reversible process to reproduce **2** from **3** was not successful.

In conclusion, we have synthesized a unique three-dimensional condensed rare-earth metal coordination polymer via hydro-(solvo)thermal reactions in water/ethanol. This structure not only exhibits high thermal stability but also can be transformed to a different structure by desorption and reabsorption of water. This unique property may contribute to the current investigations in the field of molecular sorbents, phase separation, and adsorption/desorption processes.

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Supporting Information Available: Crystallographic data for $\text{Er}_4(\text{bdc})_6 \cdot 6\text{H}_2\text{O}$: An X-ray crystallographic file (CIF). IR data of **1**, **2**, and **3** and related PXRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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